Oil Determination of Oilseed. Gravimetric Routine Method

SIXTEN TROËNG, Cereal Laboratory, The Swedish Seed Association, Svalöv, Sweden

THE SAMPLE must be comminuted without loss of oil, significant for the result obtained, and without inhomogenization of the sample. Grinding the sample in a mortar will not be feasible in a routine method. A rotating mortar has been tried (16) and found to be unsatisfactory. Milling and extraction in one operation has been made possible with the use of high-speed "blenders" (7, 2, 5, 6). These methods all require individual handling of the samples. Milling and extraction of series of samples have been introduced by Schwarze (17). As a rule however some pretreatment of the samples is common to his methods.

Experimental

Working along the lines developed by Schwarze (17), it was found possible to mill whole oil seed with steel balls and sand together with petrol by shaking the tubes in their length direction in a shaking machine. Thus the principle for simultaneous milling and extraction was clear.

Recommended Method

Special Apparatus.

1. Sieves, diam. 22 cm., round holes, 2.50, 3.00, or 3.50 mm.
2. Sample divider, model according to Analytica, European Brewery Convention 1953.
3. Shaking machine, sturdy construction, length of stroke 100 mm., 175 r/m, with cases for centrifuge tubes.
4. Centrifuge, fitted with head for 16 tubes.
5. Thermostat, waterbath, 20° ± 0.1°C., with racks for centrifuge tubes, preferably of stainless steel.
6. Hot-plate, about 45 watts/dm^2.
7. Centrifuge tubes, stainless steel, 70 ml., neck inner diam. 18 mm.
8. Steel balls, second-class balls for ball bearings, 11/16 sw. in. (17.3 mm.).
9. Stoppers, oil resistant.
10. Beakers, stainless steel, 100 ml., with grip.
11. Pipettes, 40- and 20-ml., tips with raw edge, not made smooth by melting.

Volume	Tip hole	Time of delivery (petrol)
40 ml.	2.0 mm.	6-8 seconds
20 ml.	1.8 mm.	5-6 seconds

The pipettes fitted with "Peleus" balls.

12. Dippers, 20 x 20 mm., taking 5 g. of oilseed.

Reagents.

Petrol, boiling point 96°-100°C., re-distilled if necessary. To test, four quantities of 1 g. of oil are weighed in beakers. To two of the beakers 20 ml. of petrol are added. The petrol is evaporated, and the oil is dried for 2½ hrs. at 100°C. Any significant difference in weight due to the petrol will indicate the necessity of re-distillation.

Pumice: sieved, 1.5-2.5 mm.

Analysis: the sieves are used to "skim off" coarse foreign particles. They are used for seeds in the following way:

Species	Diameter of holes
Turnip rape	2.50 mm.
Rape	3.00 mm.
White mustard, flax	3.50 mm.

The non-fat material "skimmed off" is weighed, and the figure is used to correct the values obtained in the analysis. After sieving, the sample is re-homogenized by being passed several times through a sample divider. A sample of 25-50 g. is drawn. This subsample is dried and kept in a desiccator until the analysis is resumed.

The centrifuge tubes are arranged in number sequence in the cases. For each tube 4 steel balls are taken as grinding material. "Blind tubes" without sample, 2 or 4, are run in every series. This serves as a control of the quality of the rubber stoppers and the cleaning of the tubes.

A flat bottom, preferably short-necked, 2-liter flask is filled with petrol. The temperature is adjusted to 20°C. ± 0.1°, and the flask is placed in a waterbath at 20°C. ± 0.1°.

With a pipette—to be kept vertical and handled with care—40 ml. of petrol are added to the tubes. Immediately after the discharge of the petrol into a tube, the tube is firmly closed with a stopper. On the stoppers a thick mat of felt is placed, and the lids of the cases are firmly pressed on and locked in position. The tubes are shaken in their length direction for 1 hr. The tubes are centrifuged for 10 minutes at 2,000 r/m, placed in racks, and transferred to a waterbath of 20°C. ± 0.1°.

After 15-20 minutes, when the contents of the tubes have reached 20°C., volumes of 20 ml. are transferred to tared beakers containing 5-10 grains of pumice. The pipette is fitted with a stopper so as not to dip into the sediment. The solutions are evaporated on a hot-plate and the beakers removed as soon as bubbling has ceased (perhaps a steam bath would be better). They are dried for 2½ hours at 100°C.

Calculation.

Pipetting out 20 ml. of solution from a tube to which 40 ml. of petrol have been added will give less than 50% of the total amount of oil. The volume of oil in solution has been determined for solutions of 2-10 g. of oil per 100 ml. solution at 20°C. Specific volume = 1/specific gravity.

An empirical method of calibration was considered to be most practicable.

TABLE I

Specific Volume of Oils in Solution

Oil	Specific volume	
	Pure oil	Oil in solution
Rape	1.099	1.080
White mustard	1.098	1.082
Flax	1.077	1.060
Cameline	1.086	1.065

A series of oil quantities, well distributed within the range corresponding to the oil content which is to be encountered in ordinary samples, was weighed into centrifuge tubes and the analysis was carried out in the usual way. The quantities of oil were subtracted with the weights obtained from blind samples and recalculated to pure oil, free of moisture.

The ratio of oil in the sample/oil weighed out was obtained from a diagram made up from these analyses.

The moisture was determined by drying as in the analyses (2½ hrs. at 100°C.). The blind samples varied between 0.5 and 3 mg. in these analyses. The quantities of oil were reduced to water-free oil and recalculated to the corresponding percentage of oil in a 5-g. portion.

Type of Curve Obtained.

If the oil had gone into solution without adding anything to the volume, the curves would have been of the type $Y = K \cdot X$

if a = sample portion, g.
V = volume of solvent, ml.
S = specific gravity of oil (in solution)
G = quantity of oil, weighed out, g.
P = percentage of oil

the following expression is obtained

$$P = \frac{2\,G}{1 - \frac{2\,G}{V \cdot S}} \cdot \frac{100}{a}$$

for a = 5
V = 40
S = 0.926 (rape)

$$P = \frac{741\,G}{18.52\,G}$$

The following examples show a slight difference between theoretical and empirical results.

Oil, weighed, g.	Percentage of oil (5-g. sample)	
	Theoretical	Empirical
0.86	36.08	36.00
1.00	42.29	42.25
1.15	49.06	49.25

Testing the Method

On the advice of Tedin, of the Swedish Seed Association, the testing of the method was planned as follows:

Of turnip rape, rape, white mustard, and flax 3 samples each were selected. The samples were pure strains from the Oil Seed Department. They were purified, homogenized in a sample divider, and transferred to glass containers. These samples were analyzed during 5 days with two parallels per sample each day.

Extraction analyses were made at the same time. Five-g. portions were extracted with petrol ether bp. 30°-50°C. for 6 + 4 hours in a Soxhlet apparatus or 4 + 2 hours in a Twisselmann (Butt) extractor, drying and grinding with sand between extractions.

The testing of the method was carried out in a stage of the development of the method when 10 g. of quartzite were added to each tube to act as grinding material. However quartzite was found to be unnecessary for the seeds and consequently it has been deleted in later analyses.

Results

The results have been collected in Table II. Excluding the figures obtained during the first day (when the analyst might be less trained), the average M_8 was calculated. This figure was also used in calculating the standard deviation. However, as can be seen from the table, no great discrepancies were encountered in the first-day values.

The comparatively low values for Soxhlet extraction may be due to incomplete extraction, and thus the slow rate of extraction in this type of apparatus is demonstrated.

Acknowledgment

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Prof. W. Rudorf and Dr. P. Schwarze have given attention to the problems on a visit to them at Voldagsen, Germany. Dr. Holmberg, Chief Engr. Ohlin, and Dr. Wode have discussed the method on their visits to this laboratory. Dir. Steen, Getinge, kindly supplied us with the first steel tubes. The contractors have been greatly interested in and given great assistance to the manufacture of the items necessary. Miss Anna-Stina Bäckström has made the analyses for calibration and testing of the method with good precision.

TABLE II

Oil in Dry Substance

Sample nr	Seed	The New Method				Extraction analysis	
		M_8 four days	M_2 first day	$\sigma = \sqrt{\frac{S^2}{n-1}}$ Single analysis	$\sigma = \sqrt{\frac{S^2}{n-1}}$ Average per day	Soxhlet 6 + 4 hours M_2	Twisselmann (Butt) 4 + 2 hrs. M_2
1	Turnip rape 22	40.21	39.96	0.20	0.18	39.78	40.18
2	Turnip rape 23	39.64	39.73	0.16	0.12	39.30	39.54
3	Turnip rape 24	39.97	40.05	0.20	0.13	39.35	40.17
4	Rape 28	43.69	43.64	0.12	0.07	43.35	43.66
5	Rape 29	39.05	39.05	0.30	0.10	38.60	38.83
6	Rape 87	46.07	45.99	0.23	0.21	45.62	46.32
7	White mustard 25	32.71	32.30	0.29	0.24	32.08	32.63
8	White mustard 7808	31.87	31.71	0.17	0.15	31.65	31.70
9	White mustard 8223	32.15	31.77	0.29	0.27	31.83	31.87
10	Flax C 26	44.34	44.38	0.19	0.14	43.84	44.30
11	Flax 7806	43.02	42.98	0.13	0.13	42.78	42.93
12	Flax 8965	45.67	45.69	0.16	0.05	45.03	45.65

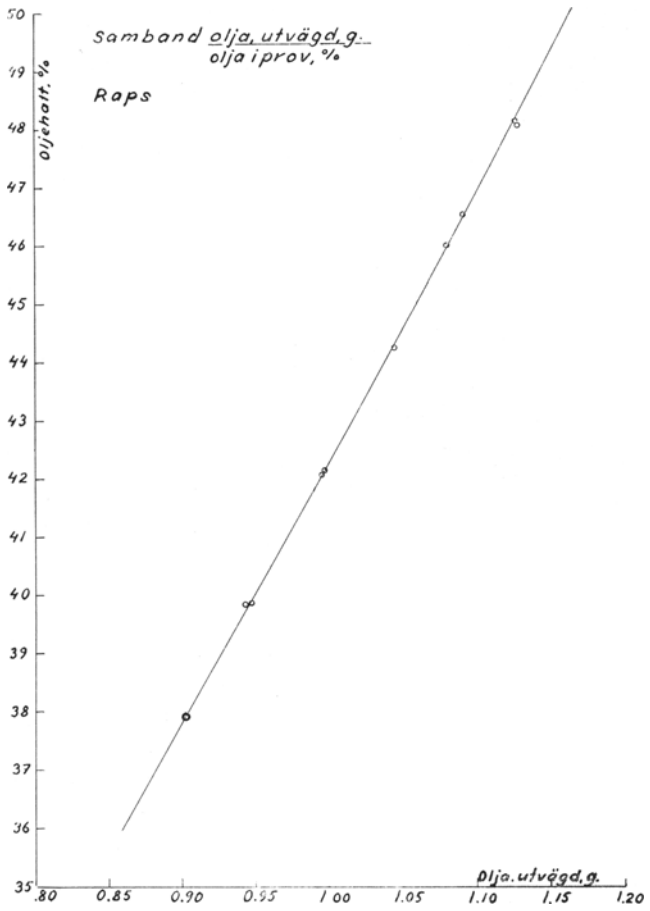

FIG. 1. Diagram for calculating percentage of oil from weight of oil.

Summary

A new method for the determination of oil on long series of oilseed is presented. It is a gravimetric method which reduces the hand labor to a minimum.

TABLE III

Analyses of Rapeseed Performed With and Without Addition of Quartzite. Oil in Dry Substance. Averages of Two Parallels.

Sample no.	The new method with quartzite		The new method without quartzite		Extraction analysis (Butt)
	Oil %	Difference from standard method	Oil %	Difference from standard method	
16,154	46.0	−0.4	46.3	−0.1	46.4
16,179	46.0	−0.3	46.3	±0	46.3
16,209	44.8	−0.6	45.2	−0.2	45.4
16,236	45.6	+0.4	46.0	−0.2	46.2
16,242	47.3	−0.6	47.4	−0.5	47.9
16,264	45.4	−0.5	45.5	−0.4	45.9
16,267	49.1	−0.3	49.0	−0.4	49.4
16,268	45.9	±0	46.0	+0.1	45.9
16,269	46.5	−0.4	46.8	−0.1	46.9
16,270	47.7	−0.1	47.7	−0.1	47.8
16,705[a]	48.2	−0.3	48.3	−0.2	48.5
Averages		−0.3		−0.2	

[a] Turnip rape also.

Testing this method on a series of pure samples of oilseed, which were analyzed for five days with two analyses on each sample every day, the standard deviation for a single analysis lay within 0.30% and for the average of two duplicates within 0.27% of oil. The difference between averages for the new method and averages of extraction analyses made with continuous extractors did not exceed 0.28% of oil.

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Measurement of Calcium Ion Suppression by Protection of Foam of Sodium Cetyl Sulfate Solutions

JOHN ROSS, L. SHEDLOVSKY, C. W. JAKOB, Colgate-Palmolive Company, Jersey City, New Jersey

BUILDERS as protective agents in the form of phosphates are being used with synthetic detergents in greater proportion and greater tonnage than they ever were with fatty acid soaps. The protection they afford enables a reasonable detersive action to be accomplished in hard water by a relatively smaller proportion of the more expensive synthetic detergent.

The measurement of the suppresion of calcium ions is important in any examination of detergency. It can also be used to evaluate technical phosphates or other builders as well as new materials for which the virtue of sequestration or calcium ion suppression is claimed.

In the following work the foam height is used as an indicator that the concentration of sodium cetyl sulfate is undiminished or, in other words, that the solution is effectively free from calcium ions. Although the foam of many synthetic detergents is not as seriously affected by the presence of calcium ion as is the foam of pure sodium cetyl sulfate, it must be remembered that builders are used for many purposes where the efficiency is affected to varying degrees by the presence of calcium ion (1, 2).

Several methods for estimating the removal of calcium ions have been previously described. Andress and Wust (3) and later Hafford *et al.* (4) used a turbidimetric titration. In the latter procedure the indicator which precipitates as calcium salt was apparently present in the phosphate tested, and both the concentration and type of phosphate which forms